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COMPREHENSIVE RESEARCH ON RICE
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PROJECT TITLE: The Environmental Fate of Pesticides Important to Rice Culture

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OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

Objective I. To characterize the natural abiotic processes governing environmental fate of pesticides in California rice fields. Emphasis for 2005 will be on photodegradation of Granite (penoxsulam, DE-638) under California rice field conditions.

Objective II. To characterize the natural biological processes governing environmental fate of pesticides in California rice fields. Emphasis for 2005 will be on the anaerobic microbial degradation of Granite (penoxsulam, DE-638) under California rice field conditions.

Objective III. To complete studies of the metabolism of Cerano 5 MEG (clomazone) by rice and watergrass. To complete laboratory studies of comparative Cerano toxicity and its interaction with possible safeners, such as piperonyl butoxide, DiSyston (disulfoton) and/or demetonS (or its analog oxydemeton-methyl). To integrate data from greenhouse studies of Cerano and potential safeners (by Albert Fischer) with laboratory research data.

SUMMARY OF 2005 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

OBJECTIVE I

Introduction

Granite (penoxsulam, DE-638) is a new herbicide designed for post-emergence control of annual grasses, sedges, and broadleaf weeds (Roberts *et al.*, 2003; Robinson, 2003). Granite, a triazolopyrimidine sulfonamide, belongs to the ALS (acetolactate synthase) inhibiting group of herbicides which are thought to have low toxicity to mammals, birds, fish, amphibians, and invertebrates, while at the same time possess the ability to stunt weeds at extremely low doses. However, some ALS inhibitors have long residual field activities and can damage non-target

plants at concentrations so low they cannot be detected by standard analytical procedures (Whitcomb, 1999). Due to its novelty, little information has been available on the environmental fate and effects of Granite.

To predict the dissipation of any pesticide in rice field conditions, information is needed on both partitioning (volatilization and soil sorption) and degradation (microbial and photochemical breakdown) processes. Therefore, this project utilized controlled laboratory experiments simulating California rice field conditions to estimate field dissipation, and the completed experiments have yielded the parameters required for a general assessment of the fate and persistence of Granite.

In 2004, the soil-water partitioning of Granite was studied by the batch equilibrium method, which is the standard procedure to characterize the soil sorption of chemicals (OECD, 2000a; Wauchope *et al.*, 2002). This method involves soil-water slurries to yield sorption values that can be used to predict soil-water partitioning under a variety of relevant environmental conditions. To this end, soil sorption values for Granite were determined as a function of soil characteristics (organic carbon content and pH; Table 1); the values allow general predictions about soil sorption of a chemical in the field, and thus its loss from field water. Four representative California rice field soils were used: Sacramento Clay, San Joaquin Loam, Stockton Clay Adobe, and Willows Clay.

As a general rule, rice pesticides have a greater tendency to volatilize in the Central Valley, with its hot dry summers, than in other growing regions with cooler climates. Therefore, in 2004 we also assessed the potential for volatilization of Granite by determining its Henry's law constant (K_H). K_H is the *air-water partitioning* ratio at equilibrium, where c_a is the concentration of the pesticide in air as moles per liter of air and c_w is the concentration of the pesticide in water as moles per liter of water:

$$K_H = \frac{c_a}{c_w} \text{ (dimensionless)} \tag{1}$$

Table 1. Soil sorption parameters of Granite and properties of test soils. Low Freundlich constants indicate an inability to sorb to soils (Jabusch and Tjeerdema, 2005).

soil	collection site	Freundlich coefficients			K_d^a	pH	% OC	K_{oc}	% OM	K_{oc}
		K_F	n	r^2						
Sacramento Clay	Schiedel Ranch 39°18'41N, 122°10'41W	0.33	0.90	1.00	0.39	6.5	1.33	30	2.25	17
San Joaquin Loam	Matthews Ranch 39°13'09N, 121°32'46W	1.10	0.93	1.00	1.21	5.3	0.50	242	0.86	141
Stockton Clay Adobe	Thompson Ranch 39°31'22N, 121°55'46W	5.00	0.99	0.98	5.05	4.6	0.74	682	1.28	395
Willows Clay	Maxwell-Dennis Ranch 39°18'41N, 122°10'41W	0.13	0.98	1.00	0.14	6.8	1.12	12	1.95	7

[a]K_d values were calculated by using equation 4 with the datasets used for the Freundlich isotherms.
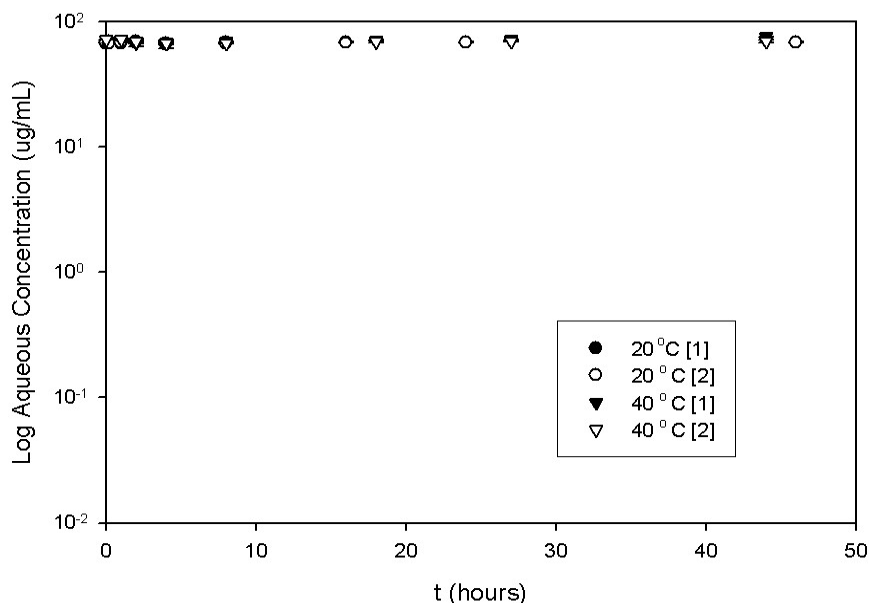
Figure 1. Air-water partitioning of Granite: dissolved concentrations vs. time in the gas-purging experiment (Jabusch and Tjeerdema, 2005).

K_H can either be estimated based on a chemical's vapor pressure (P^0, Pa) and water solubility (S; $mol \cdot L^{-1}$), or it can be experimentally determined:

$$K_H = \frac{P^0}{S} \left(Pa \cdot L \cdot mol^{-1} \right) \tag{2}$$

We used the gas-purge method (Mackay *et al.*, 1979), which is the method of choice for experimental determinations of K_H (e.g., Ten Hulscher *et al.*, 1998; Dunnivant *et al.*, 1988).

In essence, as reported in our 2004 report, both soil sorption and volatilization of Granite in rice field conditions are minimal, indicating that the herbicide will remain dissolved in water and neither dissipate by soil sorption or volatilization (Table 1 and Fig. 1; Jabusch and Tjeerdema, 2005). Therefore, its dissipation by either photolysis (Obejctive I) or microbial degradation (Objective II) was characterized, as they would represent the other potential routes of significant dissipation from rice fields.

Methods

The potential of Granite to photodegrade in simulated California rice field conditions was evaluated using both field water and the four soils most commonly used for rice cultivation in the Sacramento Valley: Sacramento Clay, San Joaquin Loam, Stockton Clay Adobe, and Willows Clay. Soil samples were collected from the top 20 cm layer of representative locations on April 27, 2004 (San Joaquin Loam) and on May 7, 2004 (Sacramento Clay, Stockton Clay Adobe, Willows Clay). Sampling sites were GIS-logged on August 6, 2004. Soils were oven-dried (100°C), disaggregated with a hammer, and homogenized using a mortar and pestle. Larger
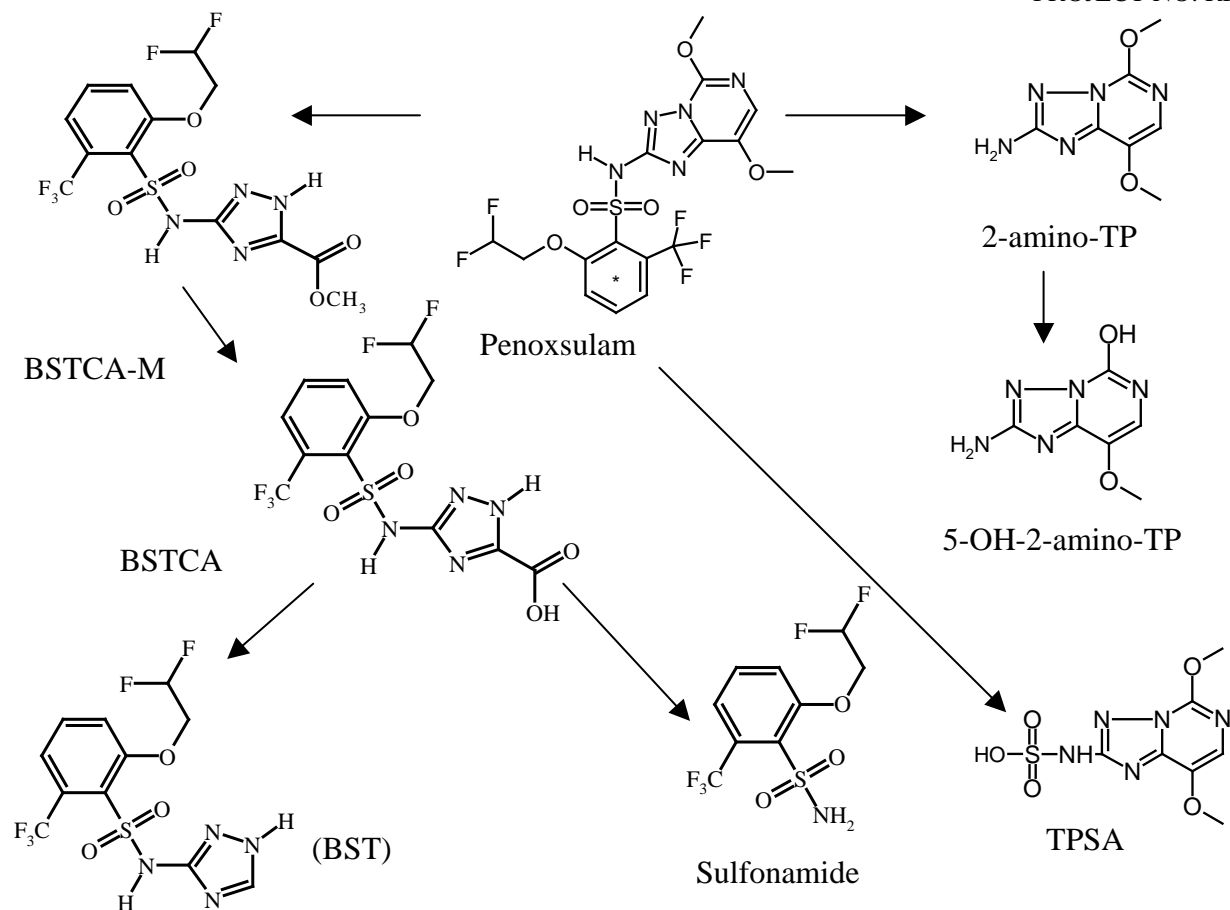
Figure 2. The photochemical degradation pathways for Granite under simulated summer California rice field conditions.

pieces of plant material were removed with forceps and the soils were sieved to a particle size ≤ 1.4 mm. The processed soil samples were kept at 5°C in a cold storage room. The soils were characterized by the DANR Analytical Laboratory at UCD.

Soil and water were prepared consisting of Granite solutions at known concentrations in 0.01 M $CaCl_2$ and soil samples of known dry weight in 50-mL Nalgene Oak Ridge Teflon FEP tubes wrapped in aluminum foil. All experimental solutions contained 200 mg L^{-1} $Hg(II)Cl_2$ as a biocide to inhibit biological degradation. Tubes were exposed to full-spectrum natural sunlight conditions, subjected to solid-phase extraction (SPE). Controls consisted of identically prepared tubes maintained in complete darkness. There was no evidence of Granite degradation in the controls.

Chemical analysis was performed with an Agilent Model 1100 LC system (Palo Alto, CA) and an API 2000™ MS/MS (MDS Sciex, South San Francisco, CA). The column was a Luna 3μ C-8 (Phenomenex, Torrence, CA). The mobile phase was 50:50:0.01 acetonitrile:methanol:acetic acid (phase A) and 100:0.01 water:acetic acid (phase B). For elution of Granite, the following elution gradient was used at a flow rate of 150 μL min^{-1} with a total run time of 20 min: start (0 min, 30:70 phase A:B); step 1 (1 min, 100:0); step 2 (8 min, 100:0); step 3 (8.1 min, 30:70); step

Table 2. Photochemical degradation rates for Granite in four rice field soils.

Soil Type	Half Life (days)	Degradation Rate Constant (per hour)	RSD (%)	Correlation Coefficient
Control Water	8.3	0.0167	5.3	0.9958
Sacramento Clay	7.9	0.0178	4.9	0.9959
San Joaquin Loam	7.4	0.0189	4.7	0.9967
Stockton Clay Adobe	5.0	0.0277	15.1	0.9822
Willows Clay	7.8	0.0180	7.3	0.9951

4 (20 min, 30:70). Analysis for Granite was performed in positive ionization mode with an electro spray interface. The injection temperature was 450°C. The Q1/Q3 ions for Granite, ^{13}C-Granite, and cloransulam-methyl were 484/193, 485/195, and 430/230, respectively. In essence, a separation and detection method for nine degradation products of Granite (provided by Dow) was developed.

Results and Discussion

The resulting degradation parameters for the four rice field soil types are presented in Table 2. The degradation rates in all soils were of the pseudo first-order type, and were characterized by short half lives. Since the process is exponential, as a rule of thumb after three half lives nearly 90% of the starting herbicide would be degraded, and it would be completely gone (100%) within 10 half lives. Thus, under typical summer rice field conditions in the Central Valley, some 90% of the herbicide would be expected to degrade via photolysis between 15 and 25 days, making Granite quite a photo-labile herbicide.

Figure 2 shows the degradation pathways for Granite under typical summer California rice field conditions. The herbicide is effectively degraded into numerous products, some via reaction with hydroxyl radical, which is first produced in water by UV light. While most, if not all, of the products are probably less toxic than the parent, it is not known if any might possess enhanced toxicity.

OBJECTIVE II

Microbial Degradation of Granite in Anaerobic Rice Field Conditions

Introduction

In general, the biodegradation study design followed OECD guidelines (OECD, 2002b); some of the methods are discussed above. Briefly, the experimental system consisted of microcosms in 60-mL wide-mouth amber flasks with a 2.5-cm layer of field soil flooded with a water layer of 1-5 cm field water. The soils used were the same as for the photodegradation study, above. The bottles were closed with a foam plug that allowed gas exchange between the microcosm and ambient air.

The microcosm system simulated an oxygenated water column over an oxygenated sediment layer that is underlain with a gradient from aerobic (oxygenated) to anoxic (oxygen-free) conditions, providing for a realistic simulation of most rice field soil conditions (OECD,

Table 3. Anaerobic biodegradation rates for Granite in four rice field soils.

Soil Type	Half Life (days)	Degradation Rate Constant (per hour)	RSD (%)	Correlation Coefficient
Sacramento Clay	7.2	0.0040	20.0	0.8957
San Joaquin Loam	13.1	0.0022	13.6	0.9313
Stockton Clay Adobe	9.6	0.0030	36.6	0.7182
Willows Clay	16.0	0.0018	33.3	0.7392

2002a;b). Thus, the results allowed estimation of the microbial rate of transformation of Granite as well as the formation and decline of transformation products in the field.

Methods

Transformation rates and pathways of microbial degradation were evaluated using the same four soils as described above. From each location, soil samples were collected from the top 20-cm layer of flooded rice fields by two methods that allowed for oxygen-free collection of submerged soils: 1) about 1 kg of water-logged soil was collected in 1-gal Ziplock bags from which the air was completely released by submerging and opening them in rice field water above the soil, and 2) at each location 10 oxygen-free soil samples were collected in 50-mL Nalgene tubes (Corning Inc., Corning, NY). To avoid exposure of the anaerobic soils to oxygen, the tubes were filled completely with water and then pushed upside-down into the sediment at a vertical angle of ca. 45°. To release water from the bottom of the sampling tube, a Teflon tube of approximately 1 m in length was inserted (for ease of usage, the Teflon tube has a nick ca. 15 cm off the end that is inserted into the Nalgene sampling tube). The soil samples were kept water logged (5°C), under oxygen exclusion and in complete darkness.

As mentioned above, experiments were conducted using aerobic water/soil system microcosms in PUF-plugged 60 mL Qorpak™ amber wide-mouth bottles (All-Pak Inc., Bridgeville, PA). The microcosms are designed to simulate flooded field conditions with an aerobic water column over an aerobic layer of field soil that is underlain with an anaerobic gradient (OECD, 2002a). Before adding XDE-638, a period of acclimation was allowed for the experimental soil/water systems to reach reasonable stability, as reflected by pH, dissolved oxygen concentration, and redox potential (OECD, 2002a). In a preliminary trial, the length of the period was determined as one week.

Dow AgroSciences has previously developed a method for extraction and analysis to determine concentrations of Granite and its metabolites in both water and soil samples by LC/MS/MS (Roberts *et al.,* 2003). Dow granted permission to use their existing proprietary method and to adapt it for use in this study. The extraction procedure in brief: soil samples were transferred to 50-mL Nalgene Oak Ridge Teflon FEP tubes and cloransulam-methyl was added as a surrogate standard to monitor extraction procedure recoveries of the analytes. Subsequently, an extraction solution of 90:10 acetonitrile/1.0 N HCl was added and the centrifuge tubes were capped and shaken for 2 h on a reciprocating shaker at 180 rpm. An aliquot of the extract was evaporated, reconstituted in 0.1 N HCl, and purified by solid phase extraction (SPE). One-mL water samples were directly applied to HLB extraction cartridges for SPE, after adding surrogate standard. For the SPE, the extract was drawn through 30-mg hydrophilic-lipophilic balanced (HLB) extraction

cartridges (Waters Corporation, Milford, MA), mounted on a vacuum manifold. The eluate was evaporated and reconstituted in HPLC mobile phase containing 5 ng mL^{-1} stable isotope internal standard ([C^{13}-Ph-UL]-DE-638). Initial recoveries for Granite were 81 ± 18 % (n = 2) for water samples and 114 ± 14 % (n = 4) for soil samples.

Chemical analysis was performed via LC/MS/MS, as described above for the photochemical degradation study.

Results and Discussion

Granite was rapidly degraded by anaerobic soil microbes in simulated California rice field conditions, producing numerous products that were similar to those produced by the herbicide's photodegradation (Fig. 2). Granite was also degraded via a pseudo first-order process, also producing relatively short half lives of degradation (Table 3). Again, since the process is exponential, after three half lives nearly 90% of the starting herbicide would be degraded via microbial action, and it would be completely gone (100%) within 10 half lives. Thus, under typical summer rice field conditions in the Central Valley, some 90% of the herbicide would be expected to degrade via photolysis between 21 and 48 days, again making Granite quite non-persistent.

In conclusion, while field dissipation of Granite under summer rice field conditions typical of the Central Valley would not be significantly influenced by either soil sorption or volatilization, dissipation would still occur rapidly – driven by both photochemical and microbial degradation.

OBJECTIVE III

Introduction

Studies of metabolism, comparative toxicity, and potential safeners of Cerano (clomazone) in rice and watergrasses are nearly completed. These two plants showed the largest difference in sensitivity to Cerano in a prior study (TenBrook and Tjeerdema, 2004). Sensitivity differences are likely due to differential activation of Cerano to the toxic 5-ketoclomazone and subsequent detoxification. A study by Culpepper *et al.* (2001) showed that the cytochrome P450 inhibitors DiSyston (disulfoton) and phorate protected cotton from Cerano toxicity as measured by growth.

In collaboration with Albert Fischer, our studies were designed to determine differences in uptake and detoxification of Cerano in rice and watergrasses, and to explore the effects of cytochrome P450 inhibiting pesticides on the toxic action of Cerano. Differential uptake and detoxification were studied by exposing plants to ^{14}C-Cerano. Metabolites were extracted and identified using high-pressure liquid chromatography (HPLC) in combination with liquid scintillation counting (LSC). To study the effects of herbicide/pesticide combinations, plants were exposed to Cerano alone and in combination with the cytochrome P450 inhibiting pesticides DiSyston or MSR (oxydemeton-methyl). Toxic effects were measured by reductions in fresh weight and β-carotene levels.

Table 4. ^{14}C mass balance for rice and EWG exposures. Portion bound or lost in extraction was determined by subtraction; all other values were measured (se = standard error; n = number of replicates). For both species, more Cerano was taken up than was volatilized or mineralized.

Rice	μCi	se	n	% of total	
Remaining in Solution	2.19	0.03	3	86.1	
Volatilized	0.01	0.00	4	0.2	
CO2	0.04	0.01	4	1.5	
Plant (total)	0.31	0.04	4	12.2	
Extracted	0.14	0.01	4		(5.4)
Bound/Lost in extraction	0.17	0.04	3		(6.8)
Total applied	2.54	0.03		100	
Watergrass					
Remaining in Solution	2.41	0.04	4	92.5	
Volatilized	0.01	0.00	4	0.2	
CO2	0.05	0.00	4	1.9	
Plant (total)	0.14	0.05	4	5.4	
Extracted	0.09	0.01	4		(3.3)
Bound/Lost in extraction	0.05	0.05	4		(2.1)
Total applied	2.61	0.01		100	

Methods

Study 1. Rice and early watergrass (EWG) were hydroponically exposed, in closed systems, to ^{14}C-labelled Cerano at 0.05 mg/L for 7 d. Radioactive residues in solution as well as volatile residues (including CO_2) were collected and quantified to provide a mass balance for Cerano in the system. Non-polar metabolites were extracted with hexane, while polar metabolites were extracted with 90:10 acetone:water. Extracts were analyzed by HPLC in combination with LSC. Two different HPLC column/solvent systems were used to confirm the identity of eluted compounds based on retention times of analytical standards.

One of the most common detoxification pathways in plants is glucose conjugation. To determine the extent of this reaction, polar extracts were further treated with β-D-glucosidase to remove glucose moieties and then HPLC analyses were repeated.

Study 2. In collaboration with Albert Fischer, a resistant (R) biotype of late watergrass (LWG) was exposed to Cerano alone and in combination with the P450 inhibitors DiSyston or MSR. Effects were measured by analysis of reduced fresh weight and β-carotene levels.

Results and Discussion

Study 1

Table 4 shows that, on a total mass basis, rice absorbed more Cerano than EWG ($p < 0.05$), but on a nmol g^{-1} basis, there was no significant difference between the two species ($p > 0.05$). Rice
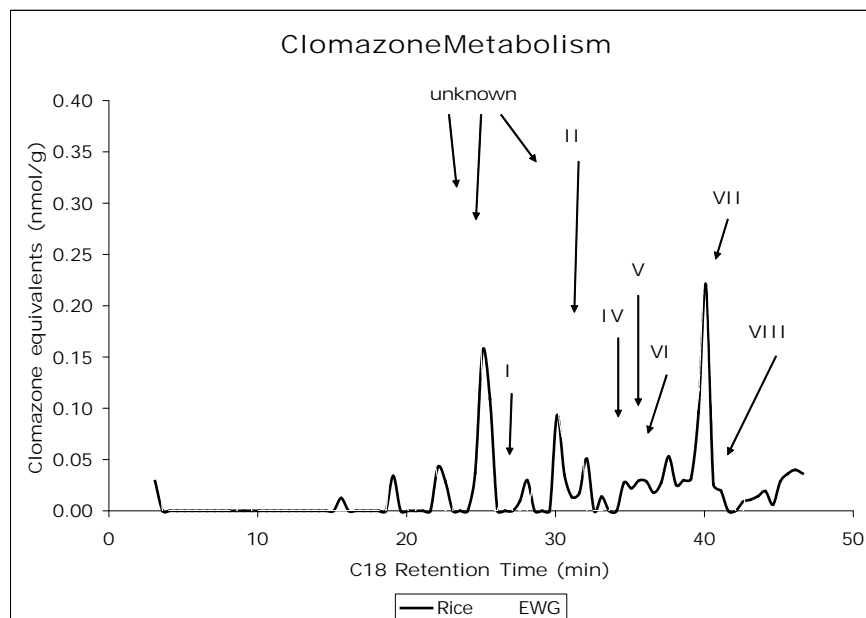
Figure 3. Chromatogram of Cerano (clomazone) and metabolites in rice and EWG as resolved by C_{18} HPLC: (I) 4',5-dihydroxy clomazone; (II) 2-chlorobenzoic acid; (III) ring-open reductive product; (IV) 3'-hydroxy clomazone; (V) 5-hydroxy clomazone; (VI) 5'-hydroxy clomazone; (VII) Cerano; (VIII) 5-ketoclomazone.

contained more extractable ^{14}C residues (7.7 ± 0.5 vs. 4.8 ± 0.5 nmol in rice vs. EWG, respectively; $p < 0.5$), but the concentration in EWG was significantly higher (4.2 ± 0.5 vs. 1.8 ± 0.1 nmol g^{-1} in EWG vs. rice, respectively; $p < 0.01$). These results can provide some explanation for the greater sensitivity of EWG to Cerano compared to rice. This is in contrast to studies which found no differential uptake between corn, soybean, smooth pigweed, and velvetleaf (Leibl and Norman, 1991), soybean and velvetleaf (Weimer *at al*., 1992), and tomato and bell pepper (Weston and Barrett, 1989).

Figure 3 compares metabolism of Cerano in rice and watergrasses via C_{18} reversed-phase HPLC. More metabolized residue was measured in EWG compared to rice (84.1% vs. 67.9%; $p < 0.01$). Both species produced hydroxylated forms, β-D-glucoside conjugates, and several other unidentified polar metabolites, but EWG generally produced higher metabolite concentrations. The concentration of the suspected active metabolite, 5-ketoclomazone, was significantly higher in EWG vs. rice ($21 + 2$ vs. $5.7 + 0.5$ pmol g-1, respectively; $p < 0.01$; Table 5). This level of metabolism can also help explain differential sensitivity since Cerano has to be activated to the toxic 5-ketoclomazone.

Differences in sensitivity to Cerano between rice and EWG appear to be due to differential metabolism, but in this case the more susceptible EWG qualitatively and quantitatively metabolized more Cerano than the more tolerant rice. This is consistent with the action of a metabolically activated herbicide. This metabolic difference could be exploited to develop herbicide safeners for use with Cerano.

Table 5. Metabolite profiles for rice and EWG; polar metabolites are shown before and after treatment with β-D-glucosidase; *p < 0.05; **p < 0.01 for changes with treatment; results are from C_{18} HPLC method (mean $\pm$ se; ∎ = not detected).

| | | **Polar** | | | | **Non-Polar** | |
Retention Time (min)	Elutes with	Rice (pmol/g) Before	After	EWG (pmol/g) Before	After	Rice (pmol/g)	EWG (pmol/g)
3.1		29 ± 2	49 ± 3**	24 ± 15	300 ± 31**	??	??
15.6		??	41 ± 7	??	??	??	??
19.1-19.6		34 ± 13	??	180 ± 39	??	??	??
21.1		??	??	??	??	??	12 ± 3
21.6		??	32 ± 4	??	??	??	??
22.1-22.6		42 ± 7	??	??	233 ± 22	??	10 ± 1
23.6-24.1		??	??	424 ± 98	94 ± 5*	??	10 ± 1
24.6-25.6		264 ± 66	??	376 ± 92	??	??	22 ± 3
27.6-28.1		29 ± 5	80 ± 12**	??	??	??	??
29.1-30.6		??	??	609 ± 162	??	??	??
31.1-31.6	III	??	33 ± 1	241 ± 17	??	12 ± 1	59 ± 9
32.1		??	32 ± 2	??	??	??	??
32.6-33.1	IV	??	51 ± 8	??	105 ± 9	??	??
33.6		??	61 ± 20	??	118 ± 2	??	??
34.1-35.1	V	53 ± 5	200 ± 32**	195 ± 39	550 ± 47**	??	??
35.6	VI	29 ± 2	31 ± 5	103 ± 18	210 ± 51	??	??
36.1-36.6	VII	26 ± 3	42 ± 7	125 ± 12	348 ± 60*	3.9 ± 0.4	13 ± 1
37.1-37.6		61 ± 4	88 ± 8*	88 ± 10	??	8.4 ± 1.6	32 ± 4
38.1		24 ± 2	??	66 ± 5	??	??	??
38.6		29 ± 5	42 ± 9	62 ± 3	??	??	??
39.1-40.6	I	121 ± 10	80 ± 8*	399 ± 17	267 ± 36*	241 ± 23	126 ± 7
41.1-41.6	VIII	??	??	??	??	**5.7 ± 0.5**	**21 ± 2**
42.6-46.6		91 ± 7	??	??	??	58 ± 2	105 ± 4
Total		832 ± 70	862 ± 45	2892 ± 221	2225 ± 106	329 ± 23	410 ± 14

Study 2

As reflected by the LWG growth data (but the β-cartoene data, which was not significant – thus not shown), both DiSyston and MSR showed significant antagonistic effects for several combinations of inhibitor plus Cerano as measured by 20-d growth (Tables 6 and 7). While Cerano alone typically reduced watergrass growth, use of a cytochrome P450 inhibitor reversed the effect, as growth generally recovered. This indicates that Cerano is oxidized to its active form by the cytochrome P450 enzymes, suggesting that cytochrome P450 inhibitors could be used as safeners with the herbicide. However, the safeners also appear to reduce the actions of Cerano on LWG, which may seriously limit its effectiveness in safening Cerano for use with rice. This effect, desirable for rice, could signify a reduction in the benefits of using safeners in rice
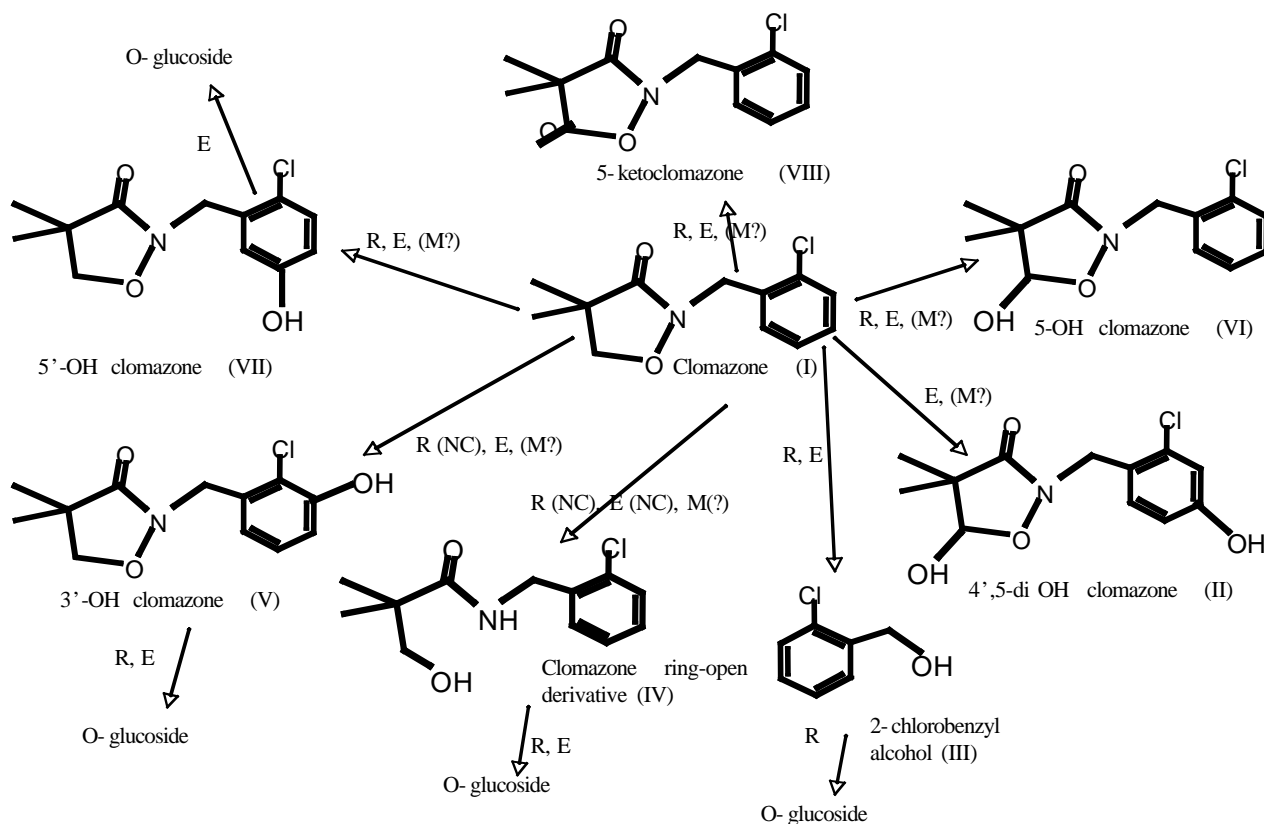
Figure 4. Proposed biotransformation pathway for Cerano in rice (R) and EWG; M (?) = possible microbial transformation; NC = not confirmed.

culture, as they would tend to also protect watergrasses and potentially reduce the selectivity of Cerano for them.

Further research is needed for mechanistic understanding of the interactions between Cerano, cytochrome P450 enzymes and cytochrome P450 inhibitors with various biosynthetic pathways that affect growth in order to best develop safeners that work to only antagonize the actions of the herbicide in rice and not watergrasses.

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Table 6. Antagonistic effects of Cerano with DiSyston on late watergrass (mean $\pm$ SE).

	Clomazone (g ai ha^{-1})	DiSyston (g ai ha^{-1})	Measured % of control	Expected % of control	p
Experiment 1	0	0	100 $\pm$ 7.2	-	-
	168	0	51.7 $\pm$ 5.2*	-	-
	337	0	45.0 $\pm$ 4.0*	-	-
	673	0	9.0 $\pm$ 4.6*	-	-
	1346	0	2.7 $\pm$ 0.7*	-	-
	0	106	98.3 $\pm$ 8.8	-	-
	0	212	91.7 $\pm$ 5.9	-	-
	0	424	76.3 $\pm$ 8.4	-	-
	0	848	55.7 $\pm$ 10.5*	-	-
	0	1696	73.0 $\pm$ 7.0	-	-
	168	106	108.7 $\pm$ 8.7	51.5 $\pm$ 9.2	< 0.05
	168	424	74.3 $\pm$ 1.7	40.1 $\pm$ 8.2	< 0.05
	168	848	88.3 $\pm$ 2.7	29.8 $\pm$ 8.7	< 0.05
	168	1696	81.3 $\pm$ 3.8	37.7 $\pm$ 5.1	< 0.05
	337	424	53.3 $\pm$ 4.7	33.7 $\pm$ 0.7	< 0.05
	673	424	21.3 $\pm$ 4.4	6.2 $\pm$ 2.6	< 0.05
	1346	106	7.3 $\pm$ 1.3	2.7 $\pm$ 0.8	< 0.05
	1346	212	13.0 $\pm$ 2.1	2.5 $\pm$ 0.7	< 0.05
	1346	424	15.3 $\pm$ 0.9	1.9 $\pm$ 0.3	< 0.05
	1346	848	9.3 $\pm$ 2.0	1.4 $\pm$ 0.2	< 0.05
	1346	1696	12.0 $\pm$ 2.1	1.9 $\pm$ 0.3	< 0.05
Experiment 2	0	0	100 $\pm$ 13.8	-	-
	673	0	14.3 $\pm$ 1.8*	-	-
	1346	0	3.0 $\pm$ 0.6*	-	-
	0	424	76.3 $\pm$ 8.4	-	-
	0	848	122.0 $\pm$ 7.9	-	-
	0	1696	97.0 $\pm$ 4.6	-	-
	673	848	27.0 $\pm$ 2.5	17.4 $\pm$ 2.2	< 0.05
	673	1696	29.7 $\pm$ 3.0	13.7 $\pm$ 1.1	< 0.05
	1346	424	10.3 $\pm$ 0.3	3.1 $\pm$ 0.6	< 0.05

*significantly different from control treatment

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Table 7. Antagonistic effects of Cerano with MSR on late watergrass (mean $\pm$ SE).

	Clomazone (g ai ha^{-1})	MSR (g ai ha^{-1})	Measured % of control	Expected % of control	p
Experiment 1	0	0	100 $\pm$ 7.2	-	-
	168	0	51.7 $\pm$ 5.2*	-	-
	337	0	45.0 $\pm$ 4.0*	-	-
	673	0	9.0 $\pm$ 4.6*	-	-
	1346	0	2.7 $\pm$ 0.7*	-	-
	0	106	60.0 $\pm$ 7.8*	-	-
	0	212	74.7 $\pm$ 4.2	-	-
	0	424	86.0 $\pm$ 14.4	-	-
	0	848	81.0 $\pm$ 15.1	-	-
	0	1696	102.3 $\pm$ 8.3	-	-
	168	106	65.0 $\pm$ 9.8	31.8 $\pm$ 7.3	0.05
	168	212	78.3 $\pm$ 10.1	39.0 $\pm$ 6.2	< 0.05
	337	106	73.0 $\pm$ 12.5	26.7 $\pm$ 2.8	< 0.05
	673	106	28.7 $\pm$ 5.4	5.2 $\pm$ 2.7	< 0.05
	673	848	26.3 $\pm$ 0.7	7.2 $\pm$ 4.0	< 0.05
	1346	212	7.7 $\pm$ 0.9	2.0 $\pm$ 0.4	< 0.05
	1346	424	8.3 $\pm$ 0.9	2.1 $\pm$ 0.1	< 0.05
	1346	848	13.0 $\pm$ 2.0	2.2 $\pm$ 0.7	< 0.05
Experiment 2	0	0	100 $\pm$ 13.8	-	-
	673	0	14.3 $\pm$ 1.8*	-	-
	1346	0	3.0 $\pm$ 0.6*	-	-
	0	106	114.0 $\pm$ 1.8	-	-
	0	212	119.0 $\pm$ 4.2	-	-
	0	424	109.0 $\pm$ 7.6	-	-
	0	848	92.3 $\pm$ 11.6	-	-
	0	1696	101.7 $\pm$ 3.8	-	-
	673	212	46.3 $\pm$ 4.3	17.1 $\pm$ 2.5	< 0.05
	673	424	43.7 $\pm$ 3.5	15.4 $\pm$ 1.2	< 0.05
	673	848	22.3 $\pm$ 1.5	13.5 $\pm$ 2.8	0.05
	673	1696	25.7 $\pm$ 2.7	14.5 $\pm$ 1.4	< 0.05
	1346	106	9.7 $\pm$ 1.2	3.4 $\pm$ 0.7	< 0.05
	1346	212	10.0 $\pm$ 1.5	3.6 $\pm$ 0.6	< 0.05
	1346	1696	9.7 $\pm$ 1.8	3.0 $\pm$ 0.6	< 0.05

*significantly different from control treatment

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CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

1. The herbicide Granite (penoxsulam) was previously found to neither significantly adhere (sorb) to rice field soils or volatilize from rice field water under simulated summer conditions. Therefore, the herbicide will remain mobile in water, as neither process would significantly contribute to field dissipation.

2. Granite was found to be highly susceptible to degradation by sunlight (photodegradation). With degradation half lives ranging from 5 to 8 days, depending on soil type, herbicide residues would approach 90% degradation within 15 to 24 days. Thus, photodegradation represents a major contributor to field dissipation.

3. Granite was also found to be highly susceptible to degradation by anaerobic soil microbes in simulated summer rice field conditions. With degradation half lives ranging from 7 to 16 days, again depending on soil type, residues of the agent would be nearly 90% degraded within 21 to 48 days. Thus, microbial degradation also represents a major contributor to field dissipation.

4. The best pesticides are those that are highly selective for the pest – and non persistent. From an environmental fate standpoint, Granite is considered to be a relatively safe herbicide for use in rice culture, as under typical summer California rice field conditions it would dissipate rapidly via photochemical and microbial degradation. Remaining residues would be expected to be minimal in water when the fields are drained.

5. In comparing the metabolism of Cerano (clomazone) between rice and watergrasses, early watergrass is capable of absorbing Cerano at almost twice the rate as rice, and produces over three times the toxic metabolite, potentially explaining the selectivity of Cerano towards watergrasses.

6. Application of the metabolic inhibitors MSR or DiSyston, in combination with Cerano, to late watergrass reduced the actions of Cerano on the watergrass, providing a safening effect by inhibiting production of the toxic metabolite. This safening effect with late watergrass may indicate a limited usefulness of safeners in rice culture.